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Hydration of α-chymotrypsin: Excess partial enthalpies of water and enzyme

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ABSTRACT

A novel method has been developed for studying simultaneously the excess partial enthalpies of wa and the enzyme in the entire range of water content. Bovine pancreatic α-chymotrypsin was used a model enzyme. The proposed method includes the measurements of the enthalpies of solution of the dr and hydrated enzyme in water at 25 °C. From these thermochemical data the excess partial enthalpies water and α-chymotrypsin were calculated. The partial quantities are very sensitive to the changes in state of water and α-chymotrypsin. A transition from the glassy to the flexible state of α-chymotrypsi accompanied by significant changes in the excess partial enthalpies of water and α-chymotrypsin. T transition appears at water weight fraction (w_1) of 0.06 when charged groups of α-chymotrypsin covered. Excess partial quantities reach their fully hydrated values at $w_1 > 0.4$ when coverage of b polar and weakly interacting surface elements is complete.

1. Introduction

The hydration of enzymes is a phenomenon of considerable fundamental importance and practical interest. It is well known that water bound to enzymes (hydration or biological water) plays a key role in determining their stability, dynamics and functions [1–3].

Water can act as a plasticizer of protein conformation [1,4]. Dehydrated proteins are rigid and glassy. In the glassy state, the dehydration-induced conformational changes and restrictions on conformational transitions cause the protein to become frozen into a broad distribution of conformational states.

Proteins undergo a glasslike transition at 25 °C and water content of about 10% (w/w) [1]. The transition from the glassy (rigid) to the flexible (elastic) state is accompanied by significant changes in the thermodynamic and structural properties. As the protein crosses the glass transition region into the flexible state, segmental motions and conformational rearrangements become possible and thermal expansivity is greatly increased.

Thermochemical studies have traditionally been of great importance in ascertaining a better understanding of enzyme–water interactions. Below a short review of the studies of hydration of enzymes is given. Since our paper presents a calorimetric study of the enzyme hydration, we have focused mostly on thermochemical results. More comprehensive reviews have been given in [1,2].

Yang and Rupley [5] studied apparent heat capacity of lysozyme as a function of water content. They identified four regions in the hydration process. Region I (dilute solution to 0.38 g water g^{-1} enzyme) corresponds to the addition of water to the fu hydrated protein. Region II (0.38–0.27 g g^{-1}) represents the co densation of water over weakly interacting surface elemer Region III (0.25–0.07 g g^{-1}) corresponds to the addition of wa to main chain carbonyls and other polar surface groups. Region (0.07–0 g g^{-1}) corresponds to hydration of charged groups.

Luscher-Mattli and Ruegg [6,7] calculated the enthalpy water sorption by lysozyme and α-chymotrypsin. The hydrati enthalpies were calculated from the temperature dependence the water vapor pressure in the range 25–40 °C. Bone studied t water sorption by lysozyme in the range 1.5–19% (g g^{-1}) [8]. C culations were done using the temperature dependence of t water vapor pressure in the range 6–46 °C. From the temperatu dependence of the water sorption isotherms in the range 17–57 Hnojewyj and Reyerson calculated differential heats of water sor tion [9]. The most important assumption of this method is that t hydration enthalpy does not depend on the temperature. Howev in strict manner, this is not correct because the heat capacities the components of hydration process (water and enzyme) depe significantly on the temperature.

Calorimetry is one of the effective methods for obtaining re able thermochemical information on the interactions of enzym with water in various environments. Smith et al. in particu have calorimetrically measured the heats of water adsorption lysozyme in the range of relative water vapor pressures from to 0.895 [10]. They obtained both the sorption isotherm and t enthalpy of hydration of the protein in the water content ran 0–18% (g g^{-1}) at 25 °C. Sorption calorimetry has been used measure the adsorption isotherm of water by lysozyme and t corresponding heat effects in the entire range of water activit [11]. Our research group has developed an experimental meth

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